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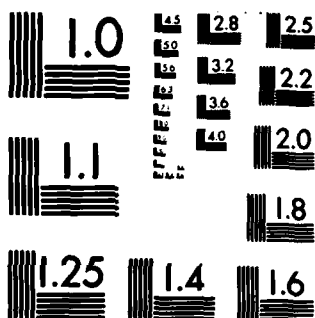
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Theoretical Studies of Kinetic
Mechanisms of Negative Ion
Formation in Plasmas

Annual Technical Report



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Theoretical Studies of Kinetic
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Annual Technical Report

Contract No. F49620-83-C-0094
Project Task 2301/A7

REPORTED BY

H. H. Michels

H. H. Michels

R. H. Hobbs

R. H. Hobbs

APPROVED BY

G. A. Peterson

G. A. Peterson

DATE

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parameters such as density, composition and temperature. A further goal was to explore new chemical sources for the production of light mass negative atomic ions. The results of this program furnish data and provide direction for more detailed investigations into the kinetics of both gas phase and gas-surface reaction rates of importance in ion source devices and provide input for reliable modeling of such systems. This investigation was carried out using quantum mechanical methods. Both ab initio and density functional approaches were employed in these studies. *Originator - supplied keywords included. -> front p.*

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FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Corporation, Research Center, East Hartford, Connecticut, under Contract F49620-83-C-0094, Project-Task No. 2301/A7. The performance period for the technical program was from 1 June 1983 through 1 June 1984. The project monitor was Captain Henry L. Pugh, Jr., USAF.

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Theoretical Studies of Kinetic Mechanisms
of Negative Ion Formation in Plasmas

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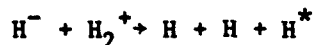
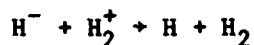
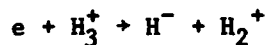
ABSTRACT

This technical program constitutes a theoretical research investigation of the kinetic mechanisms of negative ion formation in plasmas. This study was directed toward elucidating the mechanisms of the most important volume dependent reactions that occur in hydrogen-ion, $H^-(D^-)$, source devices, primarily of the Belchenko-Dimov-Dudnikov (BDD) type. The primary goal of this research program was to identify the most important reactions leading to $H^-(D^-)$ production or destruction and to estimate these reaction rates as a function of system parameters such as density, composition and temperature. A further goal was to explore new chemical sources for the production of light mass negative atomic ions. The results of this program furnish data and provide direction for more detailed investigations into the kinetics of both gas phase and gas-surface reaction rates of importance in ion source devices and provide input for reliable modeling of such systems. This investigation was carried out using quantum mechanical methods. Both ab initio and density functional approaches were employed in these studies.

STATEMENT OF WORK

The contractor shall conduct a theoretical research investigation of the electronic structure of negative molecular ions and the kinetic mechanisms of negative ion formation in plasmas. This investigation shall include the calculation of potential energy hypersurfaces for ion-atom and ion-molecule gas phase interactions that occur in magnetron-type negative ion source devices. As a new task, the contractor will perform theoretical studies of H surface adsorption to reduce the surface conversion mechanism for H^- production into a series of well characterized elementary processes. In addition, calculations shall be performed to estimate the rates of the most important volume dependent reactions leading to H^- production or destruction in such devices. Experimental data collected at LASL and IRT from their ongoing studies with negative ion source devices shall be iteratively examined and integrated with the results generated from this theoretical investigation. The computations shall be carried out with ab initio methods using electronic structure and kinetic cross-section codes that have previously been developed or modified at this Center. Specifically, this investigation shall comprise the following:

a. Quantum mechanical calculations of the potential energy hypersurfaces describing the following reactions:



b. Quantum mechanical calculations of the cross-sections and kinetic rates for the reactions specified in (a) above, including predictions of product states and branching ratios.

c. A survey of current experimental studies on negative ion source devices and comparisons of available gas phase kinetic data with the results obtained from this theoretical study.

Other gas phase reactions than those specified in (a) above may be substituted for detailed study if experimental and particle beam program directions indicate more optimum choices.

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d. Quantum mechanical calculations of the potential energy curves for Li/Li_2^- and an analysis of the probability of Li^- formation via dissociative-attachment of $e + \text{Li}_3^+$ and of $e + \text{Li}_2$.

e. Theoretical studies of the electronic structure and surface density of states for base metal (Cr, Mo, W)/alkali (Cs, Rb)/H interactions on representative base metal clusters or prototype base metal surfaces.

BACKGROUND

Recent successes in the Tokamak program and in other controlled thermonuclear research programs (Ref. 1) have focused attention on the problem of developing an efficient high-energy particle beam source. For several applications, a neutral beam with energies above 200 keV is desired. The acceleration of negative ions (primarily H^- or D^-) to such energies, followed by neutralization through a stripping reaction, appears at the present time to be the most efficient approach for producing a high energy neutral particle beam.

In another area, the feasibility of particle beams (both charged and neutral) as military weapons has been under study. The proposed endoatmospheric applications require high intensity sources and mainly focus on the problems of beam stability and propagation characteristics. Exoatmospheric applications require lower intensity sources but of very high quality. Design goals are highly collimated beams with a narrow energy spread.

A magnetron-type negative H^- source has been reported by Belchenko, Dimov and Dudnikov (BDD) (Ref. 2) that has produced H^- current densities of several $A\ cm^{-2}$. This device operates as a plasma discharge in an atmosphere of hydrogen gas with cesium or other alkalis present at ~ 0.01 percent. The mechanism for the production of H^- is believed to involve a catalyzed surface reaction whereby H^- ions are produced by transfer of electrons from Cs atoms that are adsorbed on the cathode surface (Refs. 3, 4). The detailed kinetic mechanisms of such surface reactions are still uncertain and parametric experimental studies are currently underway at LASL, LBL, IRT and at other laboratories to elucidate the mechanisms and operating characteristics of BDD and similar devices and to develop information for their scale-up to higher current densities. Diagnostics of H^- source devices are also underway at Brookhaven (Ref. 5) using beam probe and spectroscopic techniques.

Concurrent with these surface-plasma reactions are several electron- H volume-dependent processes that may lead either to the production of H^- or, in reverse, may act as important destructive processes of the negative ions after they are formed. Photodetachment experiments by Bacal and Hamilton (Ref. 6) in hydrogen plasmas indicate H^- densities 100 times larger than that predicted from simple electron attachment mechanisms. Further, these experiments indicate a nonlinear dependence of the production of H^- on electron density, at least for densities less than $10^{10}\ cm^{-3}$. Several mechanisms (Ref. 7) have been proposed to explain these volume-dependent H^- production processes but the cross-sections for many of the reactions leading to H^- are uncertain.

By a large margin, the major thrust of the development of particle beam technology has been experimental in nature. Theoretical studies of surface catalyzed reactions leading to H^- production have been undertaken by LLL (Ref. 4), but only a relatively small theoretical effort (Ref. 8) has been

directed toward detailed calculations of cross-sections for volume-dependent reactions. Because of the difficulty of conducting experiments to measure these unknown cross-sections, the development of a sound theoretical method for calculating these state-to-state processes appeared desirable. Although relatively little work of this nature has been done in the past, enough theoretical work is available to indicate that the development of such procedures can be made practical, particularly if good wave functions and potential energy surfaces are available for the interacting species.

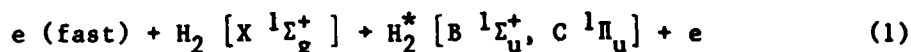
The original goal of this technical program was to delineate the most important volume dependent reactions that lead to $H^-(D^-)$ production (or destruction) and to calculate the energetics and cross-sections of such reactions as a function of system parameters. Attention was also directed toward those kinetic processes that are of importance in high pressure ion source devices, particularly of the BDD type. It was intended that this theoretical program should compliment experimental studies with negative ion source devices. A cooperative program of ongoing experimental research and our theoretical studies are of mutual benefit and result in a better understanding of the fundamental physical processes occurring in ion source devices.

A further goal of this research program was to explore new chemical sources for the production of light negative atomic ions, in particular H^- and Li^- . Studies included the formation of H^- or D^- via photodissociation of unsaturated hydrocarbon negative ions and the formation of Li^- via dissociative-attachment of electrons to molecular Li_2 .

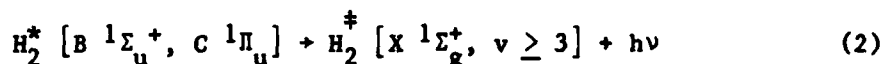
RESEARCH PROGRESS DURING THE CONTRACT YEAR

In contrast to surface catalyzed reactions, the mechanisms of most of the known volume-dependent gas phase reactions involving H^- are relatively simple to analyze, although much remains to be done to identify the state distributions for the products. A major problem, which has been addressed during the past year, has been to identify the most likely reaction kinetics leading to the formation of H^- atoms.

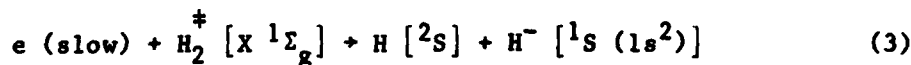
Hiskes (Ref. 10) has proposed a mechanism for the production of vibrationally excited H_2 and the subsequent production of H^- via dissociative-attachment of electrons. The initial step proposed by Hiskes involves electron excitation of ground state H_2 to an electronically excited state:



Both of these states have allowed radiative transitions to the ground state of H_2 but the displaced equilibrium separations of these excited states yield vibrationally excited H_2 upon radiative decay according to the most favorable Franck-Condon transitions:

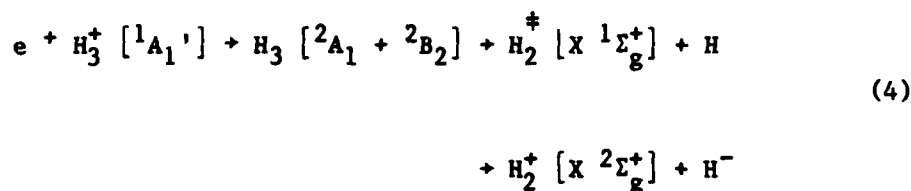


Vibrationally excited H_2 has been shown (Refs. 8, 9) to have a greatly enhanced cross-section for electron dissociative-attachment:

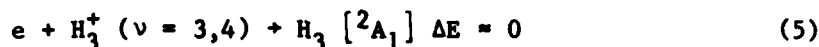


This proposed mechanism is critically dependent on the magnitude of the overall cross-section for reactions (1) and (2). Hiskes (Ref. 10) has estimated this cross section to be $\sim 10^{-18} \text{ cm}^2$, a rather low value for a volume-dependent route for the production of H^- .

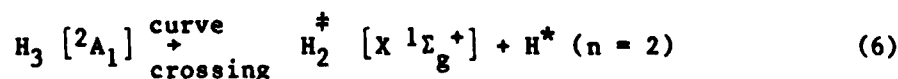
As an alternative mechanism for producing vibrationally excited H_2 , we have undertaken an analysis of the branching and product distribution for dissociative-recombination of $e + H_3^+$. The reaction scheme is as follows:



Detailed quantum mechanical calculations of these reaction surfaces have been carried out. The H_3 correlation diagram and possible low-lying dissociative-recombination reaction paths are indicated in Figs. 1 and 2, respectively. Dissociative recombination of $e + H_3^+$, as shown in Reaction (4), is exothermic by 9.3 eV to form $H_2 + H$ and endothermic by 5.4 eV to form the ion pair, $H_2^+ + H^-$. However, the detailed branching of Reaction (4) depends critically on the shape of the 2A_1 and 2B_2 hypersurfaces for H_3 for interatomic separations in the vicinity of 2-3 Å since the Coulomb attraction of the ion pair gives rise to a degeneracy in the hypersurfaces of H_3 in this region. During the past year, we have undertaken a series of ab initio calculations of the potential energy surfaces for H_3 in both C_{2v} and $D_{\infty h}$ symmetries to ascertain the character of the low-lying states. These calculations were carried out using optimized Slater-type orbital (STO) basis functions and a full CI within each symmetry group. The resultant potential energy surfaces are shown in Fig. 3. Based on these results, we find a reaction path for dissociative recombination which involves the electron attachment of $e + H_3^+$ to form a symmetric $^2A_1'$ state of H_3 which is nearly energy resonant for recombination of H_3^+ ions with three or four quanta of vibrational energy:

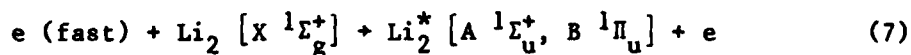


This state of H_3 correlates diabatically with the ion pair, $H_2^+ + H^-$, but exhibits many curve-crossings of the lower-lying Rydberg states of H_3 . In particular, the lowest-lying recombination pathway yields vibrationally excited H_2 molecules and electronically excited H with $n = 2$:

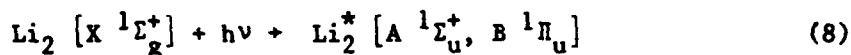


The overall recombination pathway is illustrated in Fig. 4. We find that the overall cross-section for this route to H_2^+ is $\sim 10^{-15} \text{ cm}^2$, and thus the rate of reaction (3) alone becomes rate determining. This study indicates that dissociative-recombination of vibrationally excited H_3^+ is a kinetically important volume dependent reaction for production of vibrationally excited H_2 . In high density hydrogen plasmas, relaxation of H_3^+ through collision lessens the contribution of this process in forming H_2^+ .

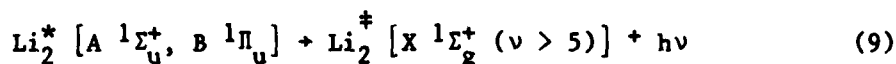
In addition to these studies of dissociative-recombination $e + H_3^+$, we have undertaken a series of calculations of Li_2^- in order to assess the energetics of this anion. McGeoch (Ref. 11) has suggested that a Li^- source should be possible through a series of reactions similar to those found for H_2 . The initial step involves the formation of the Li_2 dimer and excitation to low-lying excited states via fast electron collisions or photon pumping. The latter process is that currently being investigated by McGeoch. The reactions are:



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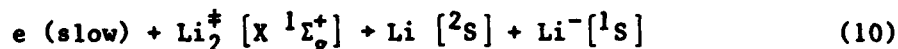


The $A \ ^1\Sigma_u^+$ and $B \ ^1\Pi_u$ state both exhibit fast radiative decay back to the ground $X \ ^1\Sigma_g^+$ state but the most favorable Franck-Condon transitions favor population of Li_2 with $v = 5$ greater:



Our present understanding of the energetics of the Li_2/Li_2^- system are shown in Figs. 5 and 6. The dashed curves in Fig. 5 were estimates based on H_2^- and the known molecular orbital structure of Li_2^- . Our most recent ab initio calculations, which indicate that the lowest $^2\Sigma_g^+$ state of Li_2^- , is slightly attractive all the way into the curve-crossing with the ground state of Li_2 , are shown

in Fig. 6. This suggests that electron dissociation-attachment is possible for this system for vibrationally excited Li_2 molecules:



The final potential energy curves governing reaction (10) are shown in Fig. 6. There is still considerable uncertainty in the location of the excited resonant states of Li_2^- , especially in the auto-ionizing region above $\text{Li}_2 + e$. The ground $[X \ ^2\Sigma_u^+]$ state is well characterized theoretically (Refs. 12, 13) but little is known about the location of the low-lying excited electronic states which connect to $\text{Li} [^2P] + \text{Li}^- [^1S]$. In addition, by analogy with H_2^- , low-lying electronic states of Li_2^- with MO configuration $(1\sigma_g^2 1\sigma_u^2 2\sigma_g 1\pi_u^2) [^2,4\Sigma_g^+]$ may, in fact, actually lie lower than some of the states shown in Fig. 5. Such states dissociate to very high atom-ion limits and their general characteristics are uncertain. The curves shown in Fig. 6 represent our best estimates at the present time but more definitive calculations are required to define the curve-crossing regions for dissociative-attachment.

The lowest $^2\Sigma_g^+$ state of Li_2^- has the molecular orbital configuration $[1\sigma_g^2 1\sigma_u^2 2\sigma_u^2 2\sigma_g]$ for large separations and was the focus of our studies of this system during the past year. At short internuclear separations, this state mixes with a second bound $^2\Sigma_g^+$ state arising from $\text{Li} [^2P] + \text{Li}^- [^1S]$ with a molecular orbital configuration $[1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g]$. This mixing at intermediate separations results in a lowering of the interaction potential for the lowest $^2\Sigma_g^+$ state. Our preliminary calculations, as shown in Fig. 5, indicate that this mixing is stronger than expected from MO considerations and lower the $^2\Sigma_g^+$ potential curve into a feasible region for dissociative-attachment to occur. A preliminary analysis of the imaginary part of the $^2\Sigma_g^+$ potential has been carried out. We find $\Gamma(R) \sim 0.01 \text{ k(R)}$ indicating that this state is mainly Feshbach in character and has a long lifetime against autoionization.

Further theoretical studies of these interactions potentials are required to define the overall reactive kinetics leading to Li^- production. A study parallel to that reported by Hiskes (Ref. 10) for H_2 has been carried out to estimate the overall cross sections for production of vibrationally excited Li_2 . In addition, theoretical studies are in progress in collaboration with Professor J. Wadehra, to estimate the low-energy electron dissociative attachment cross-section for $e + \text{Li}_2^+ \rightarrow \text{Li} + \text{Li}^-$. The results of these studies would be of value to the experimental program of McGeoch (Ref. 11) to define the overall utility of this volume-dependent source of Li^- ions.

Eleven technical papers and presentations have resulted from the research efforts conducted under this contract.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals and Books

1. "Low Temperature Dissociative Recombination of $e + H_3^+$ ". H. H. Michels and R. H. Hobbs, to be published in the Astrophysical Journal, November 1, 1984 issue, Vol. 286.
2. "Dissociative Recombination of $e + H_3^+$. An Analysis of Reaction Product Channels." H. H. Michels and R. H. Hobbs, published as a chapter in Production and Neutralization of Negative Ions and Beams, (3rd Int'l Symposium, Brookhaven, 1983), ed. Krsto Prelec, p. 118, 1984.
3. "Electronic Structure of the Helium Molecular Anion, He_2^- ." H. H. Michels, Physical Review Letters, 52, 1984, pp. 1413-1416.
4. "Electronic Structure of the Lithium Molecular Anion, Li_2^- ." H. H. Michels, to be published in Chemical Physics Letters, 1984.
5. "Vibrational Excitation of Li_2 ($X^1\Sigma_g^+$) via Electron or Photon Excitation of the $A^1\Sigma_u^+$ or $B^1\Pi_u$ State." J. M. Wadehra and H. H. Michels, to be published in Chemical Physics Letters, 1984.

B. Technical Paper and Lecture Presentations

1. "Dissociative-Recombination of $e + H_3^+$. An analysis of Reaction Product Channels." Presented at the 3th International Conference on the Physics of Electronic and Atomic Collisions, West Berlin, Germany, July 27-August 3, 1983.
2. Attended the Dynamics of Molecular Collisions Symposium, Kaiserlautern, Germany, August 2-5, 1983.
3. Attended the 8th International Seminar on Ion-Atom Collisions, Utrecht, Netherlands, August 1983.

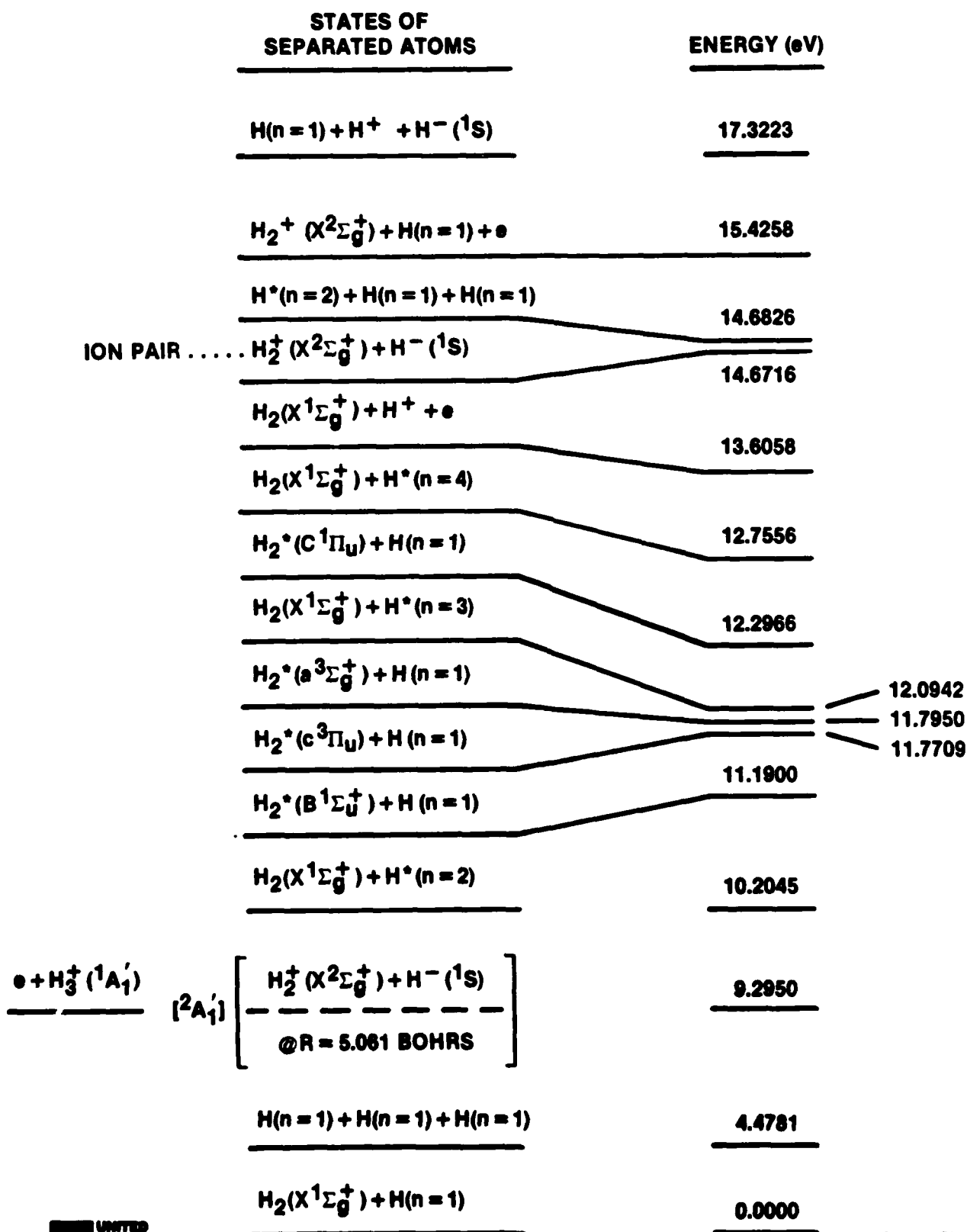
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4. "Dissociative-Recombination of $e + H_3^+$. An Analysis of Reaction-Product Channels." Presented at the 3rd International Symposium on the Production and Neutralization of Negative Ions and Beams, Brookhaven National Laboratory, New York, November 14-16, 1983.
5. " H^- and Li^- Production by Dissociative Attachment." Presented at the Neutral Particle Beam Technical Interchange Meeting II, AFWL, New Mexico, December 13-16, 1983.
6. "Electronic Structure of the Helium Molecular Anion, He_2^- ." Presented at the Molecular Spectroscopy Symposium, Ohio State University, June 11-15, 1984.

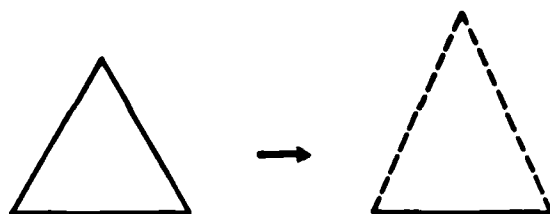
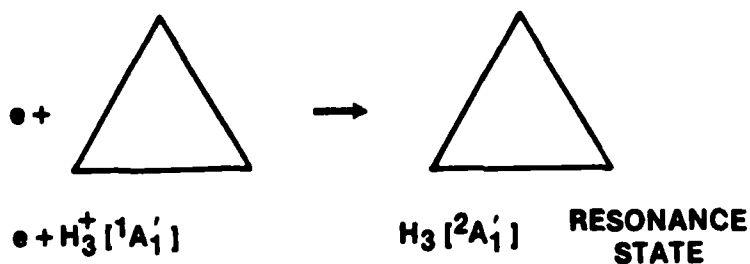
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H₃ CORRELATION DIAGRAM

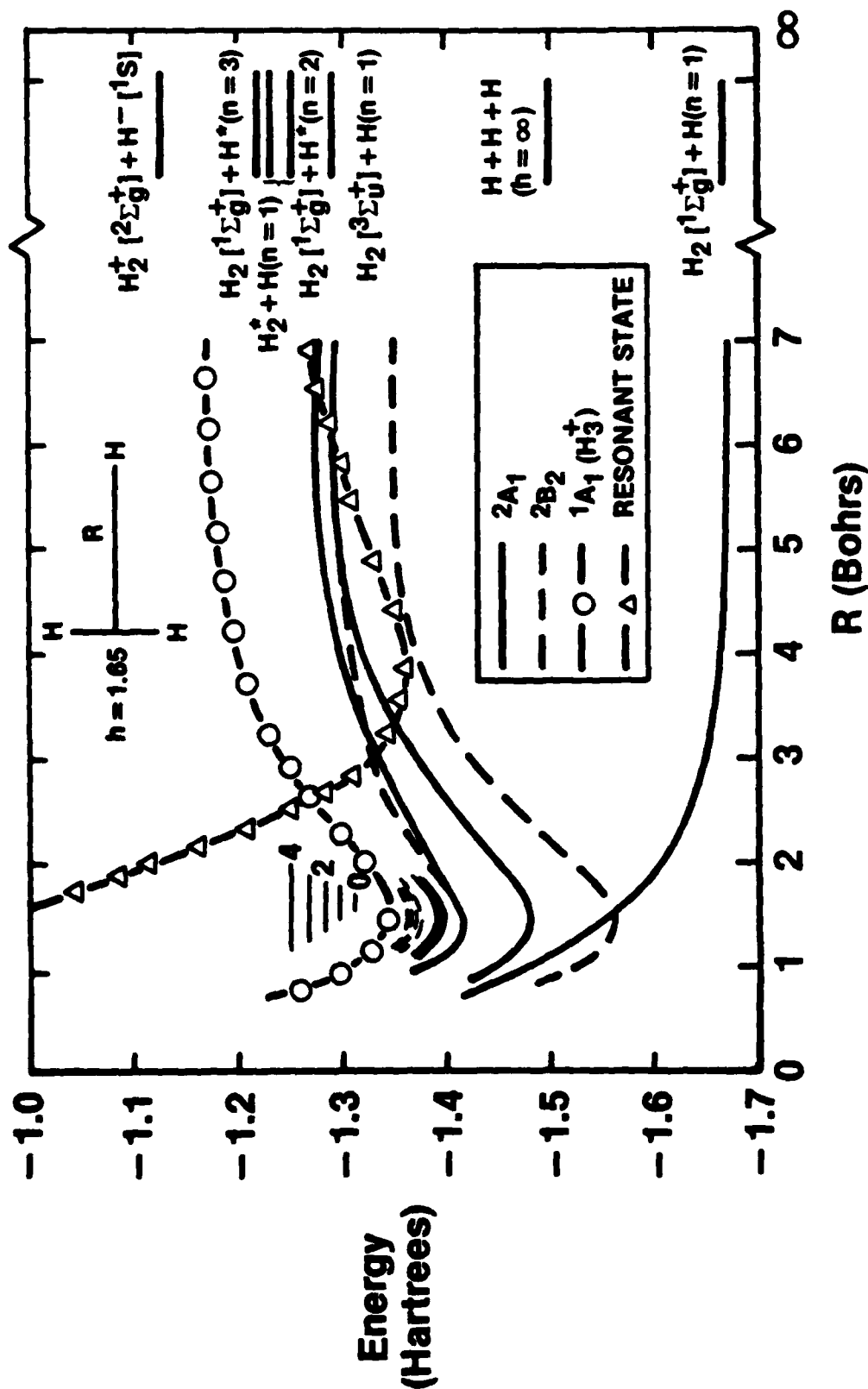


DISSOCIATIVE — RECOMBINATION REACTION PATHS

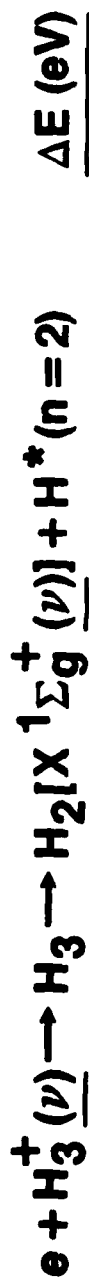


		<u>ΔE (eV)</u>
$H_3 [^2A_1']$	$\rightarrow H_2 [X \ ^1\Sigma_g^+] + H^* (n=2)$	+0.91
	$\rightarrow H_2^* [B \ ^1\Sigma_u^+] + H (n=1)$	+1.89
	$\rightarrow H_2^* [c \ ^3\Pi_u] + H (n=1)$	+2.48
	$\rightarrow H_2^* [a \ ^3\Sigma_g^+] + H (n=1)$	+2.50
	$\rightarrow H_2 [X \ ^1\Sigma_g^+] + H^* (n=3)$	+2.80
	$\rightarrow H_2 [X \ ^1\Sigma_g^+] + H^+ + e$	+4.31
	$\rightarrow H_2^+ [X \ ^2\Sigma_g^+] + H^-$	+5.38

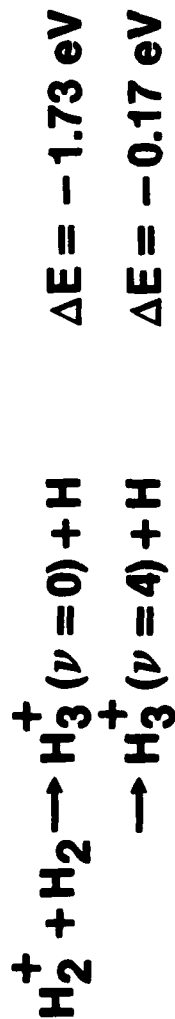
POTENTIAL ENERGY CURVES FOR H₃



$e + H_3^+$ RECOMBINATION ENERGETICS



0	0	+0.91
1	0	+0.52
2	0	+0.13
3	0	-0.26
4	0	-0.64
4	1	-0.12



RECOMBINATION PATHWAY

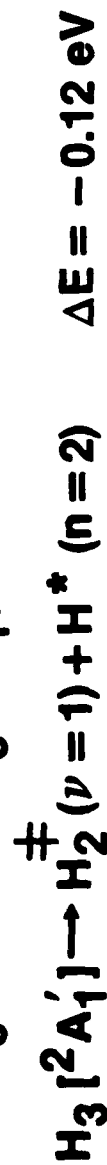
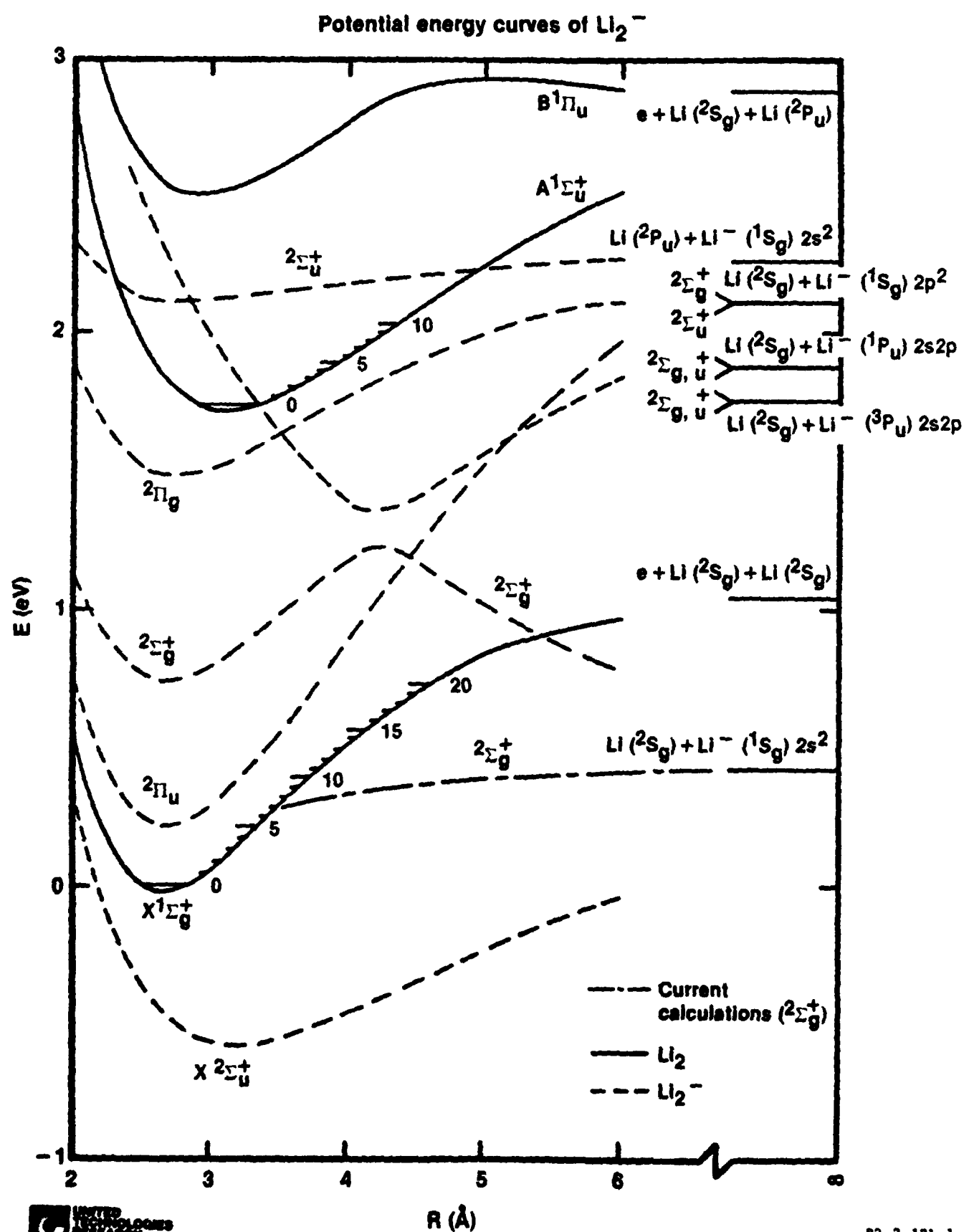
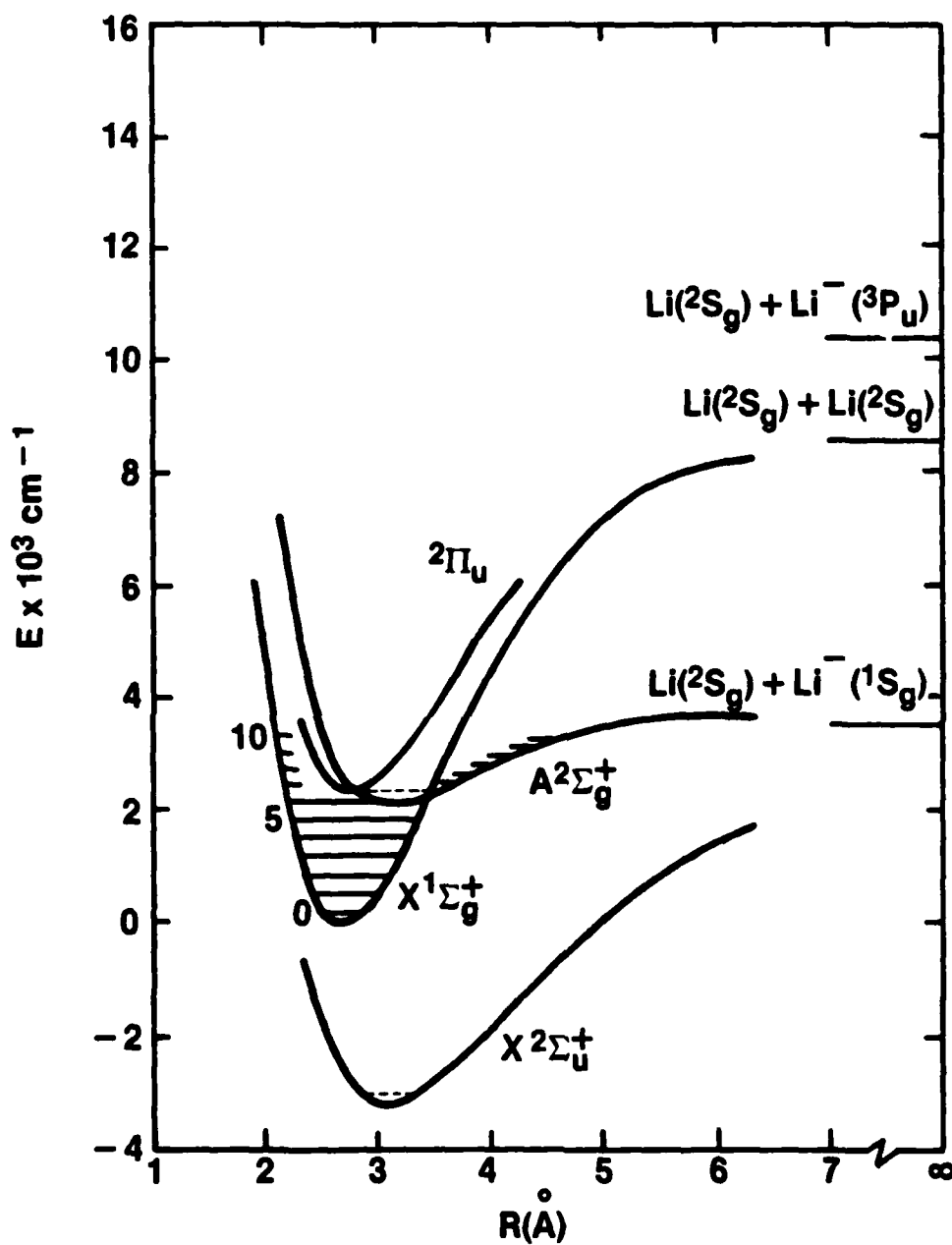


FIG. 4

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LOW-LYING POTENTIAL ENERGY CURVES OF Li_2^- 

APPENDIX A

LOW TEMPERATURE DISSOCIATIVE RECOMBINATION OF $e + H_3^+$

H. H. Michels and R. H. Hobbs*
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

Accurate ab initio calculations of the ground and excited H_3 potential energy surfaces have been carried out. These surfaces have been examined at geometries appropriate for an analysis of the reaction products of $e + H_3^+$ dissociative recombination. Direct recombination occurs through the 2A_1 resonance state which correlates diabatically to $H_2^+ + H^-$. For low collisional energies, this resonance state is accessible only to H_3^+ ions with at least three quanta of vibrational energy. Indirect dissociative recombination of $e + H_3^+$, via capture into vibrationally excited Rydberg states of H_3 , also has a very low probability since there are no effective curve crossings with the lower valence states dissociating to $H + H + H$ or $H + H_2$. We estimate that the currently accepted values of the $e + H_3^+$ recombination coefficient for interstellar conditions are two orders-of-magnitude too large.

* Supported in part by AFOSR under Contract F49620-83-C-0094.
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APPENDIX B

DISSOCIATIVE-RECOMBINATION OF $e + H_3^+$. AN ANALYSIS OF REACTION PRODUCT CHANNELS

H. H. Michels and R. H. Hobbs*
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

Accurate ab initio calculations of the ground and excited H_3 hypersurfaces have been carried out within a configuration-interaction framework. These surfaces have been examined for geometries appropriate for an analysis of the reaction products of dissociative recombination of $e + H_3^+$. Direct recombination occurs through the 2A_1 resonance state which connects diabatically to $H_2^+ + H^-$. This resonance state is accessible for low-energy electron attachment to H_3^+ ions carrying three or more quanta of vibrational energy. Under these conditions the predicted products are $H^*(n=2) + H_2^+(X^1\Sigma_g^+)$, where any excess vibrational energy in the H_3^+ ions is transferred to the product H_2 molecule. Direct dissociative recombination of H_3^+ ions in their ground vibrational state is unlikely for low collisional energies (< 6 eV) and indirect capture processes must be examined for this case.

* Supported in part by AFOSR under Contract F49620-83-C-0094.
Published as a Chapter in Production and Neutralization of Negative Ions and Beams, (3rd Int'l Symposium, Brookhaven, 1983), ed. Krsto. Prelec., p. 118, 1984.

APPENDIX C

ELECTRONIC STRUCTURE OF THE HELIUM MOLECULAR ANION, He_2^-

H. H. Michels*
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

The recently discovered He_2^- ion is examined using configuration-interaction wavefunctions constructed from an extended STO basis. We find that the $^4\Pi_g$ state of He_2^- is bound relative to the $a^3\Sigma_u^+$ state of He_2 . The calculated electron affinity is 0.233 eV compared to 0.077 eV for the $\text{He}^- [4p^0]$ atomic ion. This anion decays through the long-lived $5/2g$ component with $\tau \sim 350 \mu\text{sec}$ and the much shorter-lived $3/2g$, $1/2g$ components with $\tau \sim 10 \mu\text{sec}$.

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APPENDIX D

ELECTRONIC STRUCTURE OF THE LITHIUM MOLECULAR ANION, Li_2^-

H. H. Michels and R. H. Hobbs*
United Technologies Research Center
East Hartford, Connecticut 06108

L. A. Wright
Mission Research Corporation
Albuquerque, New Mexico 87106

ABSTRACT

The electronic structure of the ground and excited states of the Li_2^- anion has been studied using optimized CI wavefunctions. The low-lying $^2\Sigma_g^+$ state is of the Feshbach type and exhibits a near-degeneracy between $^2\Sigma_g^+$ ($v'=0$) of Li_2^- and $^1\Sigma_g^+$ ($v''=6$) of Li_2 . In contrast with the H_2^- system, we find a rich spectrum of low-lying resonant states for Li_2^- .

* Supported in part by AFOSR under Contract F49620-83-C-0094.
To be published in Chemical Physics Letters, 1984

APPENDIX E

VIBRATIONAL EXCITATION OF $\text{Li}_2(X^1\Sigma^+)$ VIA ELECTRON OR PHOTON
EXCITATION OF THE $A^1\Sigma_u^+$ and $B^1\Pi_u$ States

J. M. Wadehra
Department of Physics, Wayne State University
Detroit, MI 48202

H. H. Michels*
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

Cross sections for vibrational excitation (VE) of the $X^1\Sigma$ state of Li_2 via formation of the excited $A^1\Sigma_u^+$ or $B^1\Pi_u$ electronic states are reported. For VE through the $A^1\Sigma_u^+$ state, the cross sections are nearly constant for forming $3 \leq v'' \leq 9$ via electron collisional excitation. For photon pumping (670 nm $\leq \lambda \leq$ 700 nm) of the $A^1\Sigma_u^+$ state, levels $v'' \leq 9$ are predominantly formed. VE via the $B^1\Pi_u$ state has a lower probability.

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